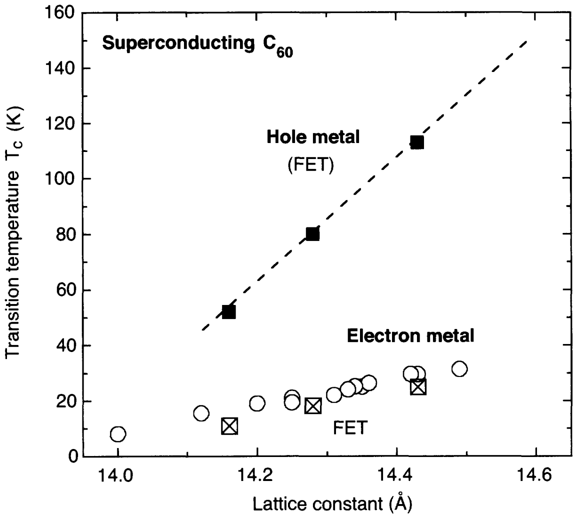

Fig. 4. Variation in T_c as a function of lattice constant for electron- and hole-doped C_{60} crystals. Square symbols are the present results using gate doping with electrons (open squares) or holes (solid squares). Open circles are for chemically doped A_3C_{60} bulk samples, where the variation of the lattice parameter is due to the different size of the ions (A).

the topmost layer of the crystal. An approximately linear increase of T_c with increasing lattice constant was observed for hole-doped intercalation compounds, pointing to a vanishing of T_c for a lattice parameter of ~13.9 to 14.0 Å. Recent theoretical considerations are in contrast to this result (*16*).

The analysis in Fig. 4 suggests that even higher values of T_c should be achievable. If the lattice parameter can be further increased by ~1%, T_c is expected to exceed 150 K. The question is how to further expand the lattice without finally losing the cohesion. Although Coulomb forces between the anions and cations provide some additional stability of the A_3C_{60} crystals, the expansion of van der Waals–bonded C_{60} with neutral molecules poses new challenges. In this context, the field-effect transistor geometry with the charged layer sandwiched in between the gate dielectric and the bulk of the crystal might provide additional advantages. It is generally thought that superconductivity in C_{60} is mediated by electron-phonon interaction. In light of T_c exceeding 100 K, it will be particularly revealing to evaluate the effective Coulomb interaction and the role of nonadiabatic pairing channels, because the Fermi energy is not much greater than the phonon energy (*12*, *13*, *17*, *18*).

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Restricting Dislocation Movement in Transition Metal Carbides by Phase Stability Tuning

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A mechanism to enhance hardness in multilayer coatings is proposed. Using the technologically important hard transition metal carbides as prototypes, although the principle is transferable also to other systems, we demonstrate, from first-principles calculations, that by suitable alloying the energy difference between several competing structures in the transition metal carbides is small or tunable. This creates multiphase/polytypic compounds with a random or controllable layer stacking sequence, systems in which the propagation of dislocations can be strongly suppressed by a large number of interfaces between structures with different glide systems, accordingly allowing the possibility of a greatly enhanced hardness. With modern thin-film technologies, it should therefore be possible to deposit such materials that will express multilayer characteristics with only minor changes in the chemical constitution of the material, which is in contrast to conventional superlattices.

Hardness is one of the most sought after material properties and one of the most important attributes of the transition metal carbides and nitrides. Hardness is important for many obvious reasons, reducing the wear of everyday objects being one and creating machining tools being another. In materials science, one distinguishes between the hardness and the strength of a material. Strength is the resistance of a material against failure, here separated into brittle and ductile failure, whereas hardness is the resistance against localized plastic deformation, microscopically corresponding to the motion of dislocations. The hardness of a material, often measured by indenter techniques, is therefore determined by how resistant the bonds in the material are against distortions and how dislocations are able to move in the system (*1*). A hard material should ideally also be ductile to maximize potential use.

In recent years, the search for novel hard materials has benefited from advances in the theoretical treatment of electronic structure in solids. The hardness of a material is not entirely given by the electronic structure readily available from density functional theory calculations, but the first factor, the straining of bonds in a material, can be modeled theoretically by calculating the elastic constants of the material.

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The second factor, the movement of dislocations in a system, is less readily accessible to calculation and simulation. The key issue here is that dislocations should be hindered from moving in the system; the dislocations need to be pinned to enhance the hardness of the system. One example of this is traditional work hardening, in which a ductile material is plastically deformed by cold working, creating a large number of dislocations with reduced mobility. Another example is the addition of secondary phases, such as precipitations, where the introduction of lattice strains can lead to a strong reduction in the mobility of dislocations. Recently, extremely hard superlattice or multilayer structures have gained a lot of attention (*1*). For example, a substantial increase in hardness has been observed for superlattices of TiN/VN (*2*, *3*). Here, the interfaces between the two nitrides tend to reduce the mobility of dislocations. Another possibility is to create a superlattice structure of nonisostructural phases, such as Mo/NbN (*1*). In this example, the different phases will exhibit different glide systems that will prevent the dislocations from moving easily through the interfaces between the phases in the superlattice. Accordingly, a controlled growth of a structure maximizing the number of interfaces between nonisostructural layers can be used to produce superhard designer materials.

In this report, we propose a way of creating enhanced hardness in transition metal carbides (TMCs), although the principle is transferable to any system, by identifying regions in the valence electron concentration (VEC) where several structures are found to have the same, or nearly the same, total energies. The TMCs and nitrides are important bulk and thin-film materials used in many technological applications because of their unique combination of properties, e.g., high hardness, high melting points, and excellent electrical conductivity (*4*). All TMCs display ductile behavior, i.e., they deform plastically, above a certain temperature, depending on the specific compound (e.g., 800°C for TiC), but dislocation movement is important also at lower temperatures (*5*, *6*). Hence, hindering dislocation movement enhances the materials properties in the TMCs at both high and low temperatures. Two comprehensive reviews of the electronic structure and physical properties have been done by Schwarz (*7*) and Johansson (*8*), and many theoretical calculations have been performed for these systems (*9*–*13*). The carbides and nitrides not only exhibit a high hardness, they can also form a variety of polytype structures. A very illustrating example of this is MoC, which is known to form at least four structures, shown in Fig. 1 and differing only in stacking sequence of atomic layers: (i) the WC structure, which is the ground-state structure for MoC and WC; (ii) the NaCl structure, which is the ground-state structure for the group IVb and Vb TMCs and a high-temperature phase in the MoC system; (iii) the TiAs structure (found in the MoC system); and (iv) the so-called η structure of MoC. From discovering a multiphase/polytypic region in the VEC, we thus propose that one can create, for example, coatings of the mentioned materials where the stacking sequence of the atomic planes will be essentially random or tunable by small controlled variations of the production parameters, such as gas flow, deposition rate, gas composition, and so forth. Such controlled deposition is possible with modern thin-film techniques, for example, physical vapor deposition (PVD) (*14*). For example, one can envisage an embodiment where the system is allowed to alternate between a cubic and a hexagonal structure. The cubic NaCl structured (B1) transition metal carbides have two primary glide planes, the {110} and the {111} planes, whereas the hexagonal WC structure has the prismatic {100} planes as glide planes (*5*, *15*). This embodiment will thus create a material with a very large number of interfaces between structures with different glide systems, and the interfaces between the different structures will hinder the propagation of dislocations, thereby drastically increasing the hardness of the material. The proposed systems therefore optimize the two factors determining hardness in a material by (i) combining the inherent strength of the bonding in the transition metal carbides, manifested in their remarkable bulk and shear moduli, and, (ii) hindering the propagation of dislocations by maximizing the number of interfaces between different slip systems. An advantage is also that this is done without changing the chemical constitution of the material, as is done in conventional superlattices.

To determine the relative phase stabilities, we calculated the total energies for the four monocarbide structures that have been experimentally verified for the 4d and 5d transition metal carbides, being those structures found in MoC and shown in Fig. 1. Because the structures of CrC and MnC are not included, as these are of a more complicated nature, the predictions for the 3d transition metal carbides are less certain. However, these structures have not been found in the 4d and 5d TMCs. The theoretical calculations are based on the local density approximation of density functional theory and hence give total energies at 0 K. For our calculations, we used a pseudopotential plane-wave method as implemented in the Vienna ab initio simulation package (VASP) (*16*, *17*). The structures were allowed to relax in volume and cell shape, while conserving the inherent symmetry of the system (*18*, *19*).

The results from our extensive calculations of phase stabilities for the group IV-VII 3d, 4d, and 5d transition metal carbides are shown in Figs. 2 to 4. The theoretical data correctly predict the equilibrium structures for all studied carbides, for example, the NaCl structure for the group IV and V carbides and the WC structure for the MoC and WC compounds (*5*,

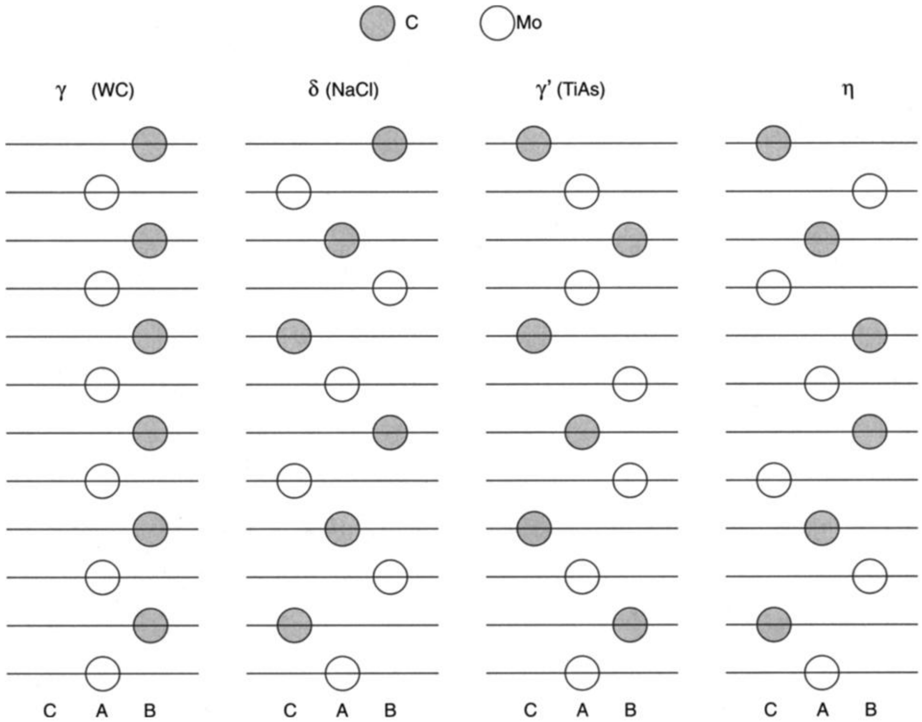


Fig. 1. The four structures of MoC can all be viewed as different stacking sequences of close-packed–like planes of metal and carbon atoms. In this view, with the close-packed site notation, the WC structure is described by *AbAb*, the NaCl structure by *AcBaCbAcBaCb*, the TiAs structure by *AbAcBaBc*, and the η structure by *AcBaCbAcBaCb* (here, we use capital letters for metal sites and small letters for nonmetal sites).

20). The difference in energies between the structures is smallest for the group VI carbides (CrC, MoC, and WC). This separation in energy indicates how easily the less stable phases may be formed and the small span in energy shows why, for example, MoC has so many stable and metastable phases whereas the other transition metal carbides do not (4). It is also seen that this span is decreased when going from the 5d to the 4d to the 3d compounds. From these figures, one can identify a region in the valence electron concentration where all four phases are found to have equal, or almost equal, energies. For the 3d TMCs, this occurs at VEC = 9.6 to 9.8, for 4d TMCs, it occurs at VEC = 9.6 to 9.7, and for 5d TMCs, it occurs at VEC = 9.5 to 9.6. It has been shown in an earlier work by Hugosson and co-workers (13) that the relative phase stabilities between the phases in MoC are also changed as a function of vacancy concentration, the order of stability between the cubic and hexagonal phase being reversed, and a similar multiphase/polytypic region may therefore also be formed in the substoichiometric group VI carbides (21). Taking into account this effect of substoichiometry, alloying a substoichiometric group VI carbide with higher transition metals opens up an alternative avenue for the realization of a multiphase/polytypic region.

Fig. 2. The relative phase stabilities for four structures of the group IV-VII 3d TMCs. The solid line of zero energy difference denotes the energy of the WC structure (the energy of the WC structure is taken to be zero).

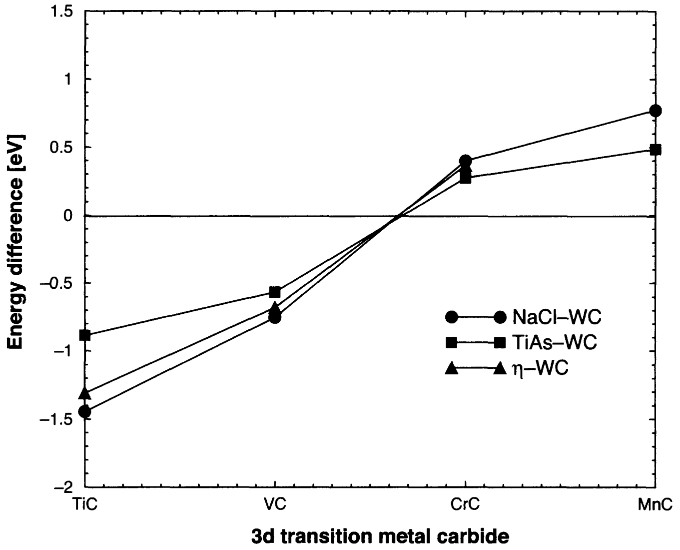


Fig. 3. The relative phase stabilities for four structures of the group IV-VII 4d TMCs. The solid line of zero energy difference denotes the energy of the WC structure (the energy of the WC structure is taken to be zero). Open symbols show the energies calculated for the ternary $Nb_{0.50}Mo_{0.50}C$ structures.

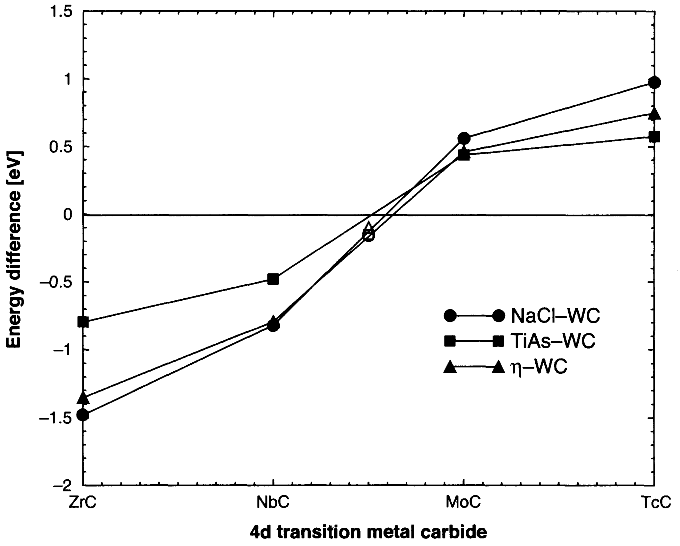
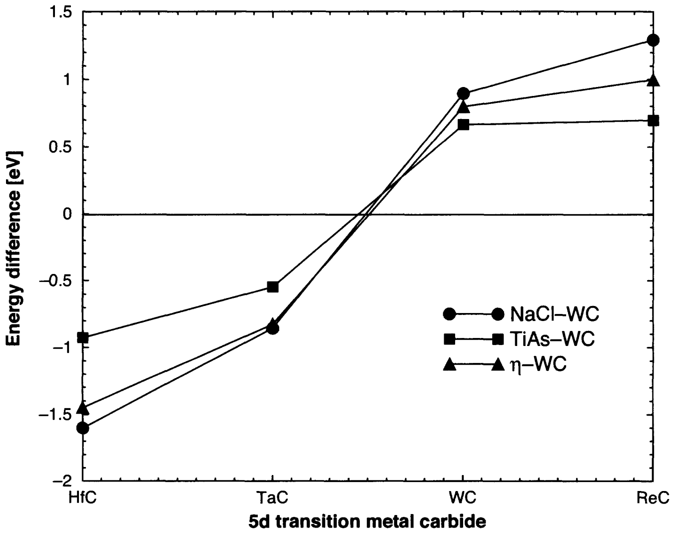


Fig. 4. The relative phase stabilities for four structures of the group IV-VII 5d TMCs. The solid line of zero energy difference denotes the energy of the WC structure (the energy of the WC structure is taken to be zero).



Because all four studied structures are variations of stacking sequences of metal and nonmetal planes, another way of looking at the results from our studies is that the stacking fault energy goes to zero for certain values of VEC. Hence, the proposed multiphase/polytypic region may also manifest itself in the occurrence of a large number of stacking faults or as a lack of long-range periodicity.

To control the present predictions, using linear interpolations between the total energies, we also calculated the phase stabilities for the ternary $Mo_{0.50}Nb_{0.50}C$ alloy and the isovalent ternary alloy $Tc_{0.25}Nb_{0.75}C$. The results for ternary $Mo_{0.50}Nb_{0.50}C$ are shown in Fig. 3, and the energies of ternary $Tc_{0.25}Nb_{0.75}C$ are found to be almost the same (not shown). It is found that the linear interpolations are accurate and that the predicted turnover in phase stabilities is a function of the VEC. The relative phase stabilities can therefore be tuned by suitable alloying of transition metals. The linear interpolations between the phase stabilities of different compounds, which is only shown for neighboring elements of the same period, can easily be made for elements of different periods. Likewise the required VEC to produce low structural energy differences may be reached by higher orders of alloying than ternary carbides, for example, quaternary carbides, and so forth.

Little experimental work is, to our knowledge, reported on the hardness of ternary transition metal carbides, but in experimental studies of the ternary nitride system $Ti_xV_{1-x}N$, Knotek and co-workers found a considerable increase of hardness for a virtually stoichiometric compound with 29 atomic % vanadium (22). Although they do not report on finding any increase in stacking faults or other evidence of the so-called multiphase region, this is at the same VEC as that suggested in this work for the carbides. The multiphase/polytypic region can be expected to occur also in the nitrides because the electronic structure of the nitrides is generally very similar to that of the carbides, with only simple rigid band shifts. Boxman and coworkers also report a substantial increase of hardness (from 25 GPa up to 50 GPa) in $Ti_xNb_{1-x}N$ for x slightly below 0.5 (*23*).

In conclusion, we have identified regions in valence electron concentration where several phases of the 3d, 4d, and 5d transition metal carbides have the same or similar total energies. From this finding, we suggest that compounds may be deposited, using modern thin-film techniques, where the stacking sequence of atomic layers is essentially random or controllable through minor changes of the production parameters. Further experimental studies of the proposed systems are highly desired. Examples of possible embodiments include coatings deposited at the calculated optimum VEC, where several structures have the same energies, with essentially random stacking sequences or a large number of stacking faults. A second alternative is one where layers of two alternating structures are deposited, by controlled variations in deposition conditions, creating superlattices differing only in structure but not in chemical composition. The multiphase/polytypic regions and the consequent hardening mechanism predicted here are also expected to be found in other systems, for example, the transition metal nitrides. The hardness of, for example, coatings from such multiphase/polytypic, or stacking-fault–rich, compounds with a large number of different glide-systems suppressing the propagation of dislocations is predicted to be substantially enhanced over that of traditional transition metal carbide/nitride coatings.

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19. For the 4d TMCs, the results from the pseudopotential plane wave method were also compared with those from a more accurate full-potential method where the Kohn-Sham equation is solved without making approximations for the shape of the effective potential or to the charge density (*24*). Comparing the energies obtained from the two methods, the phase stability differences were found to be very similar, varying within 10%.
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Stability and Structure of $MgSiO_3$ Perovskite to 2300-Kilometer Depth in Earth's Mantle

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Unexplained features have been observed seismically near the middle (~1700-kilometer depth) and bottom of the Earth's lower mantle, and these could have important implications for the dynamics and evolution of the planet. $(Mg,Fe)SiO_3$ perovskite is expected to be the dominant mineral in the deep mantle, but experimental results are discrepant regarding its stability and structure. Here we report in situ x-ray diffraction observations of $(Mg,Fe)SiO_3$ perovskite at conditions (50 to 106 gigapascals, 1600 to 2400 kelvin) close to a mantle geotherm from three different starting materials, $(Mg_{0.9}Fe_{0.1})SiO$ enstatite, $MgSiO_3$ glass, and an $MgO+SiO_2$ mixture. Our results confirm the stability of $(Mg,Fe)SiO_3$ perovskite to at least 2300-kilometer depth in the mantle. However, diffraction patterns above 83 gigapascals and 1700 kelvin (1900-kilometer depth) cannot presently rule out a possible transformation from *Pbnm* perovskite to one of three other possible perovskite structures with space group *P2₁/m*, *Pmmn*, or *P4₂/nmc*.

Knowledge of the phase relations and crystal structures of lower mantle materials are essential for evaluating seismic observations (*1–3*) of the deep mantle and their geochemical and geodynamic implications (*2*, *4*). The stability and structure of $(Mg,Fe)SiO_3$ perovskite have been controversial over the last decade. Knittle and Jeanloz (*5*) confirmed the stability of orthorhombic $(Mg,Fe)SiO_3$ perovskite to 127 GPa using x-ray diffraction (XRD) on temperature-quenched samples. However, Meade *et al.* (*6*) reported observation of an orthorhombic-to-cubic phase transformation and dissociation to $(Mg,Fe)O+SiO_2$ on the basis of XRD studies of laser-heated samples at 60 to 70 GPa. The dissociation reaction was supported by Saxena *et al.*, who performed diffraction studies on both temperature-quenched (*7*) and high-temperature (*8*) samples laser heated at 60 to 90 GPa. In contrast, Raman measurements on temperature-quenched samples (*9*) and XRD measurements on laser-heated samples (*10*, *11*) were reported to show the stability of orthorhombic $MgSiO_3$ perovskite at these conditions. The origin of the discrepancy between these results remains controversial (*13*, *14*). The primary issues include the homogeneity of heating, stress conditions, transformation kinetics, and the possibility of chemical reactions.

The structure of SiO_2 at lower mantle conditions is also important, not only because of the possible existence of free silica in the mantle but also because of its effect on the relative stability

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